

U.S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER 33808F147 U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/831575
INTERNATIONAL APPLICATION NO. PCT/FR99/02744	INTERNATIONAL FILING DATE 9 November 1999	PRIORITY DATE CLAIMED 13 November 1998
TITLE OF INVENTION	POLYMERS FLUORINATED BY POLYMERISATION IN MINI-EMULSION	
APPLICANT(S) FOR DO/EO/US	Dennis Tembou Nzudie, et al.	
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input checked="" type="checkbox"/> is transmitted herewith. b. <input type="checkbox"/> has been transmitted by the International Bureau (see accompanying PCT Form 308). c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)). a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11. to 16. below concern other document(s) or information included: 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: a. PCT Request (PCT/RO/101) (in French) b. Notification of Transmittal of the International Preliminary Examination Report (PCT/IPEA/416) (in French); c. International Preliminary Examination Report (PCT/IPEA/409) (in French) c. International Search Report PCT/ISA/210 (attached to WO 00/29457)(in French) e. Applicant's Reply to Written Opinion dated December 15, 2000 (in French)		

(Page 2)

U.S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

33808F147

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known,
see 37 CFR 1.9)

09/831575

17. ☒ The following fees are submitted:

CALCULATIONS

PTO USE ONLY

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO \$860.00

International preliminary examination fee paid to USPTO
(37 CFR 1.482) \$690.00No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international
search fee paid to USPTO (37 CFR 1.445(a)(2)) \$710.00Neither international preliminary examination fee (37 CFR 1.482) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,000.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(2)-(4) \$100.00**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the
earliest claimed priority date (37 CFR 1.495(e)).

\$---

Claims

Number Filed

Number Extra

Rate

Total Claims 8 -20 = --- x \$18.00 ---

Independent Claims 2- 3 = --- x \$80.00 ---

Multiple dependent claim(s) (if applicable) + \$270.00 ---

TOTAL OF ABOVE CALCULATIONS =

\$ 860.00

Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be
filed. (Note 37 CFR 1.9, 1.27, 1.28).

SUBTOTAL =

\$ 860.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the
earliest claimed priority date (37 CFR 1.492(f)).

TOTAL NATIONAL FEE =

860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied
by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property.

+

TOTAL FEES ENCLOSED =

860.00

Amount to be
refunded \$

charged \$

a. ☒ A check in the amount of \$ 860.00 to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit
Account No. 02-4300.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b))
must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

Frederick F. Calvetti
NAME

28,557

REGISTRATION NO.

Date: May 11 2001

A..y. Docket No.
33808F147

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JC08 Rec'd PCT/PTO 11 MAY 2001
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Dennis Tembou Nzudie, et al.

International PCT Application No.: PCT/FR99/02744

International Filing Date: 9 May 1999

US Serial No.: To Be Assigned

Group Art Unit: To Be Assigned

Filed: : May 11, 2001 (Herewith)

Examiner: To Be Assigned

For : POLYMERS FLUORINATED BY POLYMERISATION IN MINI-EMULSION

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Prior to or concurrent with calculation of the filing fees, please amend this application as follows.

IN THE SPECIFICATION:

On page 1, after the title, please add the paragraph heading "Field of the Invention";

On page 1, after the first paragraph, please add the paragraph heading "Background of the Invention";

On page 4, line 3, please add the paragraph heading "Description of the Invention";

On page 10, line 6, please add the paragraph heading "Examples";

On page 19, beginning on line 23, please add the new paragraph.

FORTRAN 5/25/99

IN THE CLAIMS:

Applicants have attached to this Amendment documents entitled "Amended Claims" and "Marked-up Copy of the Previous Claims". Please replace present claims 1-7 in this application with amended claims 1-7 shown in the document entitled "Amended Claims". Please add new claim 8 as shown in the document entitled "Amended Claims".

REMARKS

Entry and consideration of this Preliminary Amendment are respectfully requested prior to or concurrent with calculation of the filing fees. This Preliminary Amendment is being filed to correct improper multiple dependencies. As so amended, the claims are submitted as appearing in proper multiple dependent form. No new matter has been added by this amendment.

Examination on the merits is awaited.

AUTHORIZATION

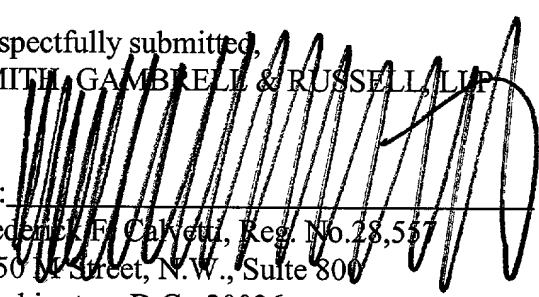
No additional fee is believed to be necessary.

The Commissioner is hereby authorized to charge any additional fees, which may be required for this amendment, or credit any overpayment to Deposit Account No. 02-4300, Order No. 33808.147.

In the event that an extension of time is required, or which may be required in addition to that requested in a petition for an extension of time, the Commissioner is requested to grant a petition for that extension of time which is required to make this response timely and is hereby

authorized to charge any fee for such an extension of time or credit any overpayment for an extension of time to Deposit Account No. 02-4300, Order No. 33808.147.

Respectfully submitted,
SMITH, GAMBRELL & RUSSELL, LLP

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May 11, 2001

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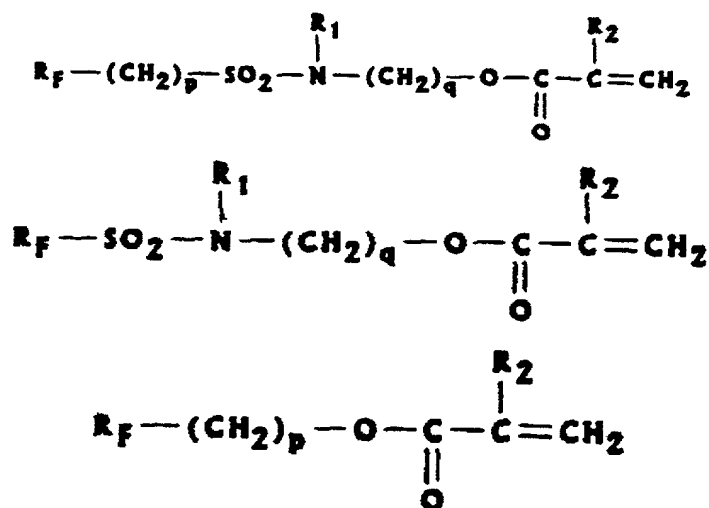
CLAIMS

1. (Amended) Process for producing
fluorinated polymers by miniemulsion polymerization in
5 two stages comprising
- a) emulsification of a mixture of monomers
comprising:
- from 20 to 99.9% by weight of at least one
monomer selected from fluorinated (meth)acrylic
10 monomers (A),
- from 0.1 to 15% by weight of at least one
monomer selected from acrylamide and its compounds,
including N-methylolacrylamide, and
- from 0 to 65% by weight of at least one
15 monomer selected from nonfluorinated acrylic or vinyl
monomers (B),
- using energetic emulsifying treatment,
including ultrasound, colloid mill or high-pressure
homogenizer, and
- 20 b) polymerization of the said mixture at a
temperature ranging from 20 to 100°C using radical
initiators,
- the level of organic cosolvent being less
than 0.2% by weight of the total weight of the
25 emulsion.
2. (Amended) Process according to Claim 1,
wherein the mixture of monomers is stabilized by at
least one surfactant selected from the group comprising
nonionic, anionic or cationic surfactants, including

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polyethoxylated sulphasuccinate compounds or quaternary ammonium compounds.

3. (Amended) Process according to Claim 1, wherein the fluorinated monomer A is selected from the group comprising the monomers corresponding to the following formulae:



in which R_F represents a perfluorinated radical with a linear or branched chain comprising 2 to 20 carbon atoms, p and q , which are identical or different, each represent an integer ranging from 1 to 20, R_1 represents a linear or branched alkyl radical comprising from 1 to 4 carbon atoms and R_2 represents a hydrogen atom or a methyl radical.

4. (Amended) Process according to claim 1, wherein the monomer B is selected from the group comprising:

- C_1 - C_{22} alkyl (meth)acrylates
- (meth)acrylates, the radical of which carries an oxyethylenated linkage

- acrylic and methacrylic acids.

- peroxides

- azo compounds, such as 4,4'-azobis

6. (Amended) Aqueous dispersion comprising
ed polymers obtained according to the process
1, the content of organic cosolvent of which
than 0.2% by weight of the total weight of the
and the level of coagulum being less than 1%
of the total weight of monomers.

8. (New) Process according to claim 3,
the integer is from 1 to 4.

09/831575

JC08 Reg'd PCT/PTO 11 MAY 2007

MARKED UP COPY OF THE PREVIOUS CLAIMS

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CLAIMS

1. Process for producing fluorinated
polymers by miniemulsion polymerization in two stages
5 comprising

a) [the] emulsification of a mixture of
monomers comprising:

from 20 to 99.9% by weight of at least one
monomer [chosen] selected from fluorinated

10 (meth)acrylic monomers (A),

from 0.1 to 15% by weight of at least one
monomer [chosen] selected from acrylamide and its
[derivatives] compounds, including [such as] N-
methylolacrylamide, and

15 from 0 to 65% by weight of at least one
monomer [chosen] selected from nonfluorinated acrylic
or vinyl monomers (B),

using energetic emulsifying [means]
treatment, [such as] including ultrasound, colloid mill
20 or high-pressure homogenizer, and

b) [the] polymerization of the said mixture
at a temperature ranging from 20 to 100°C using radical
initiators,

the level of organic cosolvent being less
25 than 0.2% by weight of the total weight of the
emulsion.

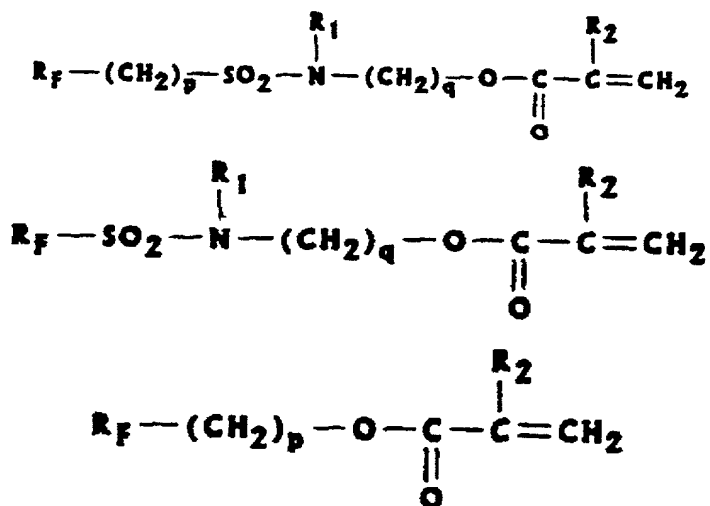
2. Process according to Claim 1, wherein
[characterized in that] the mixture of monomers is
stabilized by at least one surfactant [chosen] selected

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from the group comprising nonionic, anionic or cationic surfactants, [such as] including polyethoxylated sulphosuccinate [derivatives] compounds or quaternary ammonium [derivatives] compounds.

- 5 3. Process according to Claim 1 [or 2],
[characterized in that] wherein the fluorinated monomer
A is [chosen] selected from the group comprising the
monomers corresponding to the following formulae:

10



in which R_F represents a perfluorinated radical with a linear or branched chain comprising 2 to 20 carbon
atoms, p and q, which are identical or different, each
15 represent an integer ranging from 1 to 20 [and
preferably from 1 to 4], R₁ represents a linear or
branched alkyl radical comprising from 1 to 4 carbon
atoms and R₂ represents a hydrogen atom or a methyl
20 radical.

4. Process according to [one of the
preceding claims] claim 1, [characterized in that]
wherein the monomer B is [chosen] selected from the
group comprising:

- C₁-C₂₂ alkyl (meth)acrylates
- (meth)acrylates, the radical of which carries an oxyethylenated linkage
- vinyl monomers, [such as] including vinyl chloride or vinyl acetate
- acrylic and methacrylic acids.

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5. Process according to [one of the preceding claims] claim 1, [characterized in that] wherein the initiator is [chosen] selected from the group comprising:

- peroxides
- persalts, [such as] including persulphates
- azo compounds, such as 4,4'-azobis (4-cyanopentanoic acid).

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6. Aqueous dispersion [of] comprising fluorinated polymers [as may be] obtained according to the process of [any one of the preceding claims] claim 1, the content of organic cosolvent of which is less than 0.2% by weight of the total weight of the emulsion and the level of coagulum being less than 1% by weight of the total weight of monomers.

25

7. [Application of the aqueous dispersion of Claim 6 in the] [h]Hydrophobic and oleophobic treatment of [various] substrates comprising treatment of, [such as] leather, textiles, fitted carpets, paper and construction materials with an aqueous dispersion of the polymer of claim 6.

- acrylic and methacrylic acids.

- peroxides

- persalts, including persulphates

- azo compounds, such as 4,4'-azobis

6. (Amended) Aqueous dispersion of

7. (Amended) Hydrophobic and oleophobic

8. (New) Process according to claim 3,

8. (New) Process according to claim 3,
wherein the integer is from 1 to 4.

TOP SECRET 5/5/80

FLUORINATED POLYMERS BY MINIEMULSION POLYMERIZATION

The invention relates to the field of aqueous emulsions and in particular to a process for the preparation of aqueous emulsions of fluorinated polymers.

Fluorinated copolymers are used in various applications, in particular in the hydrophobic and oleophobic treatment of various substrates, such as textiles, leather or paper. These fluorinated copolymers are generally prepared by copolymerization in an organic solvent or according to the aqueous emulsion polymerization technique. For reasons of environmental constraints, they are generally prepared by aqueous emulsion copolymerization. For hydrophobic and oleophobic coating applications, these copolymers are obtained from at least one perfluorinated acrylic monomer and at least one nonfluorinated monomer, generally an alkyl acrylate or methacrylate.

The copolymerization of perfluorinated monomers according to the conventional emulsion technique is a technically difficult problem. This is because the strong hydrophobicity of these monomers greatly decreases, on the one hand, the contribution of the initiation of the polymerization in the aqueous phase and, on the other hand, the diffusion of these monomers from the storage drops to the growing

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particles. As a result of these particular properties of perfluorinated acrylic monomers, the use of a water-soluble organic solvent is necessary when they are employed in producing an aqueous emulsion. This solvent
5 has to be a good solvent for monomers and must not cause the polymer formed to precipitate, as is the case with certain alcohols.

The most widely used solvent is acetone (see, for example, Patents FR 1,532,053 or FR 2,202,515).
10 However, safety and transportation constraints are prompting a large number of producers to market products without a flashpoint. It is obviously possible, if the surface-active formulation has been carefully selected, to distil off the solvent used in
15 the copolymerization.

However, this decreases the productivity and results in an additional cost with regard to energy consumption, on the one hand, and confers poor stability over time on the emulsion, on the other hand.

20 The use of nonflammable solvents, such as ethylene glycol, propylene glycol and their derivatives, is disclosed in Patent FR 2,175,332 but these compounds generally exhibit a poor solvating power and must be used in combination with acetone. In
25 some commercial fluorinated emulsions, acetone has been replaced by excellent solvents with a high flashpoint, such as N-methylpyrrolidone or γ -butyrolactone. The use

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of heavy diols, such as dipropylene glycol, pentanediol, hexanediol and tripropylene glycol, in producing fluorinated acrylic emulsions without a flashpoint is disclosed in Patent JP 60.40182. However, it turns out that such emulsions exhibit a number of drawbacks related to the low volatility of the solvents, such as:

difficult drying of textile and leather articles, which it is impossible to bring to high temperature, and/or

the lack of crosslinking of the copolymer on textiles, due to the incomplete drying of the solvent and to the presence of residual hydroxyl groups.

Whatever the solutions introduced by persons skilled in the art in terms of choice of solvent, it transpires that problems arise:

- of volatile organic compounds, resulting in pollution, safety and transportation risks if the solvent cannot be distilled off,

- of productivity and of an additional cost with regard to energy consumption, if the formulation comprises a solvent of low boiling point which is distilled off at the end of polymerization.

Furthermore, the conventional emulsion presents a problem of stability and of yield insofar as emulsion polymerization results in the formation of a

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high level of coagulum (1-8%), which coagulum has to be destroyed.

According to the invention, the term "coagulum" is understood to mean the polymer in the form of a flock which is not stabilized and which sediments in the polymerization reactor, in contrast to the polymer present in the latex particle, which polymer is stabilized in a colloidal fashion by surfactants.

The problem which the invention seeks to solve is the development of an aqueous emulsion of fluorinated polymers which does not comprise volatile organic compounds, which is stable and which is devoid of coagulum, while observing industrial requirements such as economy in energy and productivity.

The solution has been found by virtue of a specific combination comprising

1) the use of a process known as the miniemulsion polymerization process, without the use of organic cosolvent, and

2) the judicious choice of a mixture of monomers necessarily comprising acrylamide or one of its derivatives.

The process is based on a first stage of specific emulsification of the water/monomer/surfactants mixture using an energetic means, such as ultrasound, colloid mill or high-pressure homogenizer,

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thus generating fine droplets of monomers in the water. The emulsification stage is followed by a polymerization stage.

The process of the invention is distinguished from conventional processes for the manufacture of perfluorinated emulsions by, on the one hand, a level of organic cosolvent in the formulation of less than 0.2% by weight of the emulsion and by, on the other hand, a level of coagulum of less than 1% by weight of the total weight of monomers. It thus exhibits the advantage of being more productive and of generating little in the way of volatile organic compound, a source of pollution.

Thus, by using the polymerization technique known as the miniemulsion polymerization technique, which technique is known in the literature for the polymerization of numerous vinyl and acrylic monomers and in particular an acrylic monomer with a longer or shorter alkyl chain, perfluorinated acrylic monomers can be copolymerized with nonfluorinated monomers, with the following advantages:

- no use of organic cosolvent and therefore fewer volatile organic compounds, no loss in productivity related to distillation and no additional cost with regard to energy consumption,

- a higher yield, as coagulum is not formed, even at high levels of incorporation of perfluorinated monomers,

- no use of cosurfactant which is a fatty compound of low solubility in water (hexadecanol, hexadecane) commonly used in miniemulsions (which can disturb the final properties).

One of the subject-matters of the invention is a process for producing fluorinated polymers by miniemulsion polymerization comprising the polymerization of a mixture of monomers, which monomers are dispersed in water and which mixture is stabilized by at least one surfactant, characterized in that the level of organic cosolvent in the reaction mixture is less than 0.2% by weight of the total weight of the emulsion.

The term "fluorinated polymers" according to the invention is understood as meaning polymers comprising at least 20% by weight of units derived by polymerization of at least one fluorinated monomer.

The process of the invention is based on two stages comprising

a) - the emulsification of a mixture of monomers comprising:

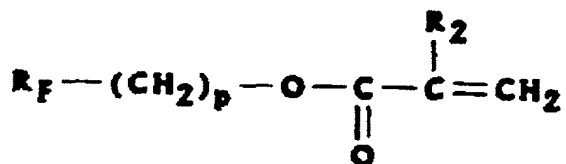
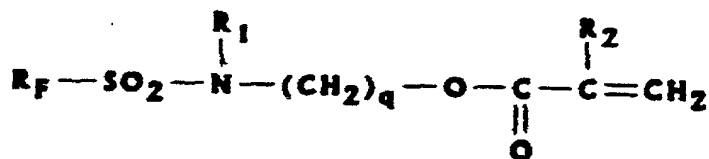
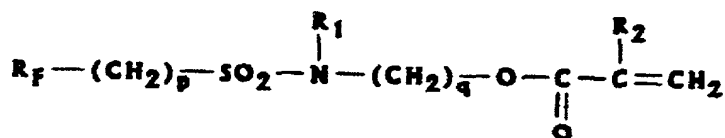
from 20 to 99.9% by weight of at least one monomer chosen from fluorinated (meth)acrylic monomers (A),

from 0 to 65% by weight of at least one monomer chosen from nonfluorinated (meth)acrylic or vinyl monomers (B),

from 0.1 to 15% by weight of at least one polar monomer (C),
 5 using energetic emulsifying means, such as ultrasound, colloid mill or high-pressure homogenizer, and

b) - the polymerization of the said mixture at a temperature ranging from 20 to 100°C using radical
 10 initiators.

The monomers A are chosen from fluorinated (meth)acrylic monomers corresponding to the following formulae:



15 in which R_F represents a perfluorinated radical with a linear or branched chain comprising 2 to 20 carbon atoms, p and q , which are identical or different, each
 20 represent an integer ranging from 1 to 20 and preferably from 1 to 4, R_1 represents a linear or branched alkyl radical comprising from 1 to 4 carbon

atoms and R_2 represents a hydrogen atom or a methyl radical.

The nonfluorinated monomers (B) are generally alkyl acrylates or methacrylates, such as, for example, butyl methacrylate, 2-ethylhexyl methacrylate and stearyl and behenyl acrylates and methacrylates, acrylates and methacrylates carrying an oxyethylenated linkage, such as ethyl triglycol methacrylate, or vinyl monomers, such as vinyl chloride, vinylidene chloride or vinyl acetate.

Mention may be made, among the polar monomers (C), of N,N-dimethylaminoethyl or N-tert-butylaminoethyl methacrylates and acrylates and their quaternized derivatives, acrylic and methacrylic acids, or monomers carrying a sulphonic acid or hydroxyl group, such as hydroxyethyl or hydroxypropyl acrylates and methacrylates.

Crosslinking agents are generally used to attach the copolymer to the substrate and to render it insoluble in solvents. They are acrylamide derivatives, such as N-methylolacrylamide and N-methylolmethacrylamide, or chlorohydroxypropyl acrylate or methacrylate.

The surfactants used are anionic or cationic surfactants, such as sulphosuccinate and quaternary ammonium derivatives, for example sodium bis(tridecyl)sulphosuccinate.

They are optionally used in combination with nonionic surfactants.

The molecular masses are adjusted using chain-transfer agents, such as mercaptans, or by the technique for introduction of the monomers. The copolymerization can be initiated at between 20 and 140°C by means of water-soluble or organosoluble initiators of peroxide type (such as hydrogen peroxide), persalt type (such as persulphates) or azo type, such as 4,4'-azobis(4-cyanopentanoic acid) or azobis(amidinopropane) hydrochloride or azobisisobutyronitrile.

The polymerization is preceded by a stage of emulsification of the mixture comprising the monomers, the water and the surfactants. It is important to carry out this emulsification by energetic emulsifying means, such as ultrasound or homogenizers of the Manton-Gaulin type or a colloidal mill. The mechanical energy contributed by these devices makes it possible to shear the mixture and to form fine monomer droplets stabilized by the surfactant. These fine droplets of monomers are sites of polymerization generating polymer particles with comparable sizes (50-500 nm).

The emulsions of fluorinated polymers according to the invention can be used in the hydrophobic and oleophobic treatment of a great variety of substrates, such as textiles, leather, paper or

construction materials. They can be applied, after dilution in water, by padding, steeping, coating or spraying. They can be formulated with various additives, such as fixing resins, catalysts, antistatic agents, antifoaming agents or fungicides.

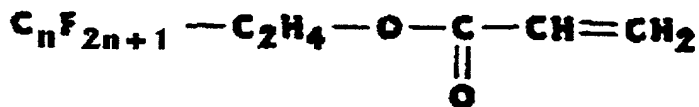
The following examples illustrate the invention without limiting it. Except when otherwise indicated, the parts and percentages are expressed by weight.

10 Example 1

a) preparation of the latex

The following are introduced into a 1000 parts by volume reactor which is heated by a thermostatically controlled jacket and is equipped with an anchor stirrer and a reflux condenser:

- 480 parts of demineralized water
- 0.12 part of borax ($\text{Na}_2\text{B}_2\text{O}_5$)
- 3.99 parts of sodium bis(tridecyl)sulpho-succinate
- 8.34 parts of a mixture of polyfluorinated acrylates of formula:



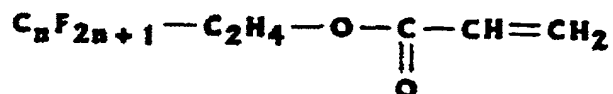
where n is equal to 8, 10, 12 and 14 in respective ratios by weight of 63:25:10:2.

25 The mixture is brought to 65°C with stirring for 30 minutes and then subjected to ultrasound (Branson Sonifier) for one minute. The following are

added with stirring to this mixture which has been subjected to ultrasound:

- 58.6 parts of 2-ethylhexyl methacrylate
- 0.36 part of methacrylic acid
- 5 - 1.26 parts of N-methylolacrylamide
- 59.8 parts of a mixture of polyfluorinated

acrylates of formula:



where n is equal to 8, 10, 12 and 14 in respective
10 ratios by weight of 63:25:10:2.

This mixture is subjected to ultrasound (Branson Sonifier) for one minute and then homogenized with a high-pressure homogenizer (Microfluidizer), 6 passes being carried out at 60°C.

15 The miniemulsion thus obtained is composed of fine droplets of monomers having a mean particle diameter of the order of 100-200 nm. It is transferred into a 1000 parts by volume reactor which is heated by a thermostatically controlled jacket and is equipped
20 with an anchor stirrer and a reflux condenser. This miniemulsion is brought to 88°C while purging with nitrogen and the polymerization is initiated with 0.84 g of potassium persulphate dissolved in 7 g of water. An equivalent amount of initiator solution is
25 run continuously into the reactor for one hour. The polymerization is continued for an additional hour. The

nitrogen purging is maintained throughout the duration of the polymerization.

A coagulum-free perfluorinated copolymer latex is obtained, which copolymer has the following composition by mass: 53.4% of perfluorinated units, 45.8% of 2-ethylhexyl methacrylate, 0.3% of methacrylic acid and 0.47% of N-methylolacrylamide. The solids content is 20% and the mean particle diameter is 130 nm.

10 b) Application to leather

The perfluorinated copolymer latex obtained is diluted in water at ambient temperature until an aqueous solution is obtained comprising 1% of active materials.

15 This solution is subsequently sprayed crosswise onto leather samples using a Volumair T 21 sprayer.

The amount deposited is on average 130 g/m². After drying for 24 hours at ambient temperature, the leather samples are evaluated in the following way:

Oleophobicity tests

The oleophobicity is measured according to the test described in "AATCC Technical Manual", test method 118 (1992), which evaluates the non-wettability of the substrate by a series of oily liquids of decreasing surface tensions. The grading of the treated substrate is defined as the maximum value of the test

liquid which does not wet the substrate. The test liquids employed in the evaluation are listed in the following table:

Grading	Test liquids for measuring the oleophobicity	Surface tension at 25°C (mN/m)
1	Nujol	31.5
2	Nujol/n-hexadecane (65/35 by volume)	29.6
3	n-hexadecane	27.3
4	n-tetradecane	26.4
5	n-dodecane	24.7
6	n-decane	23.5
7	n-octane	21.4
8	n-heptane	19.8

5

Hydrophobicity tests

The hydrophobic effect is measured using test solutions numbered 1 to 10 and composed of water/isopropanol (IPA) mixtures in the following proportions by weight:

10

Test solutions	Water	Isopropanol
1	90	10
2	80	20
3	70	30
4	60	40
5	50	50
6	40	60
7	30	70
8	20	80
9	10	90
10	0	100

These tests consist in depositing drops of these mixtures on the treated substrates and in then
 5 observing the effect produced. The grading is carried out by giving, as the value, the number corresponding to the solution which has not penetrated or wetted the substrate after being in contact for 30 seconds.

In this example, the treated leather samples
 10 are lamb skin. The results of this treatment are recorded in the table below:

	AATCC 118	Water/IPA
Treated	4	5
Untreated	0	0

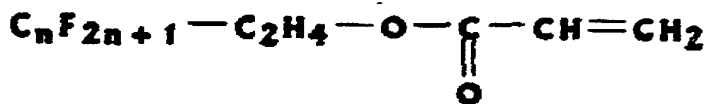
This table shows the notable effectiveness of this product.

Example 2

a) preparation of the latex

5 The following are introduced into a 1000 parts by volume reactor which is heated by a thermostatically controlled jacket and is equipped with an anchor stirrer and a reflux condenser:

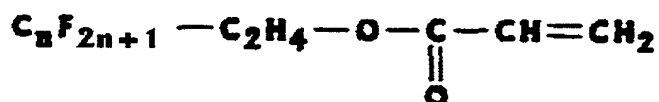
- 480 parts of demineralized water
- 10 - 0.12 part of borax ($\text{Na}_2\text{B}_2\text{O}_5$)
- 3.99 parts of sodium bis(tridecyl)sulpho-succinate
- 8.34 parts of a mixture of polyfluorinated acrylates of formula:



15 where n is equal to 8, 10, 12 and 14 in respective ratios by weight of 63:25:10:2.

The mixture is brought to 65°C with stirring for 30 minutes and then subjected to ultrasound (Branson Sonifier) for one minute. The following are added with stirring to this mixture which has been subjected to ultrasound:

- 28.58 parts of 2-ethylhexyl methacrylate
- 0.27 part of methacrylic acid
- 25 - 0.95 part of N-methylolacrylamide
- 90.2 parts of a mixture of polyfluorinated acrylates of formula:



where n is equal to 8, 10, 12 and 14 in respective ratios by weight of 63:25:10:2.

This mixture is subjected to ultrasound
 5 (Branson Sonifier) for one minute and then homogenized with a high-pressure homogenizer (Microfluidizer), 6 passes being carried out at 60°C.

The miniemulsion thus obtained is composed of fine droplets of monomers having a mean particle
 10 diameter of the order of 100-200 nm. It is transferred into a 1000 parts by volume reactor which is heated by a thermostatically controlled jacket and is equipped with an anchor stirrer and a reflux condenser. This miniemulsion is brought to 88°C while purging with
 15 nitrogen and the polymerization is initiated with 0.84 g of potassium persulphate dissolved in 7 g of water. An equivalent amount of initiator solution is run continuously into the reactor for one hour. The polymerization is continued for an additional hour. The
 20 nitrogen purging is maintained throughout the duration of the polymerization.

A coagulum-free perfluorinated copolymer latex is obtained, which copolymer has the following composition by mass: 77.1% of perfluorinated units,
 25 22.4% of 2-ethylhexyl methacrylate, 0.2% of methacrylic acid and 0.4% of N-methylolacrylamide. The solids

content is 20% and the mean particle diameter is 120 nm.

b) Application to leather

With the conditions described in Example 1 being repeated, the results obtained for Example 2 are expressed in the following table:

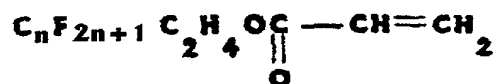
	AATCC 118	Water/IPA
Treated	4	4
Untreated	0	0

Example 3

10 a) Preparation of the latex

The following are introduced into a 1000 parts by volume reactor which is heated by a thermostatically controlled jacket and is equipped with an anchor stirrer and a reflux condenser:

- 15 - 670 parts of demineralized water
- 13 parts of dicocodimethylammonium chloride
- 12 parts of a mixture of ethoxylated alkylphenol with an HLB of 15
- 20 - 200 parts of a mixture of polyfluorinated acrylates of formula:



where n is equal to 8, 10, 12 and 14 in respective ratios by weight of 63:25:10:2

- 65 parts of stearyl methacrylate
- 8.5 parts of N-methylolacrylamide as a 48%
solution in water

- 9.2 parts of N-methylolmethacrylamide as a
5 60% solution in water

- 0.27 part of n-dodecyl mercaptan.

This mixture is brought to 65°C without
stirring for 30 minutes, then subjected to ultrasound
(Branson Sonifier) for one minute, then homogenized
10 with a high-pressure homogenizer (Microfluidizer), 6
passes being carried out at 60°C.

The miniemulsion thus obtained is composed of
fine droplets of monomers having a mean diameter of the
order of 150-200 nm. It is transferred into a 1000
15 parts by volume reactor which is heated by a
thermostatically controlled jacket and is equipped with
an anchor stirrer and a reflux condenser. This
miniemulsion is brought to 70°C while purging with
nitrogen and the polymerization is initiated with 2.03
20 parts of azobisisobutyronitrile dissolved in 20 parts
of water. The polymerization takes place in two hours.

After cooling, a coagulum-free perfluorinated
copolymer latex is obtained, which copolymer has the
following composition by mass: 70.7% of perfluorinated
25 units, 23% of stearyl methacrylate, 3% of N-methylol-
acrylamide and 3.3% of N-methylolmethacrylamide. The
solids content is 33% and is brought to 20% by diluting

with water. The mean diameter of the particles is 150 nm.

b) Application to textiles

A padding bath comprising 25 g/l of the
 5 fluorinated copolymer latex obtained above and 1.5 g/l
 of acetic acid in water is prepared at ambient
 temperature. The fabrics are subsequently padded in
 this bath with a degree of expression of the order of
 50%. After drying, the fabrics are treated for one
 10 minute at 160°C in a Benz thermal curing device.

The fabrics thus treated are subsequently
 tested with regard to oleophobicity and hydrophobicity.
 The oleophobicity is tested according to the AATCC 118
 test described above. The hydrophobicity is evaluated
 15 according to a test of resistance to wetting by water
 used to monitor the water-repellent finishing of the
 fabric (Spray Test according to AATCC Technical Manual,
 Test Method 22, 1972).

A polyamide (PA) fabric was treated.

20 The highly advantageous performance of this
 product is shown in the table below.

	AATCC 118	Spray Test
PA	6	100

CLAIMS

1. Process for producing fluorinated
polymers by miniemulsion polymerization in two stages
5 comprising

a) the emulsification of a mixture of
monomers comprising:

from 20 to 99.9% by weight of at least one
monomer chosen from fluorinated (meth)acrylic monomers

10 (A),

from 0.1 to 15% by weight of at least one
monomer chosen from acrylamide and its derivatives,
such as N-methylolacrylamide, and

from 0 to 65% by weight of at least one
15 monomer chosen from nonfluorinated acrylic or vinyl
monomers (B),

using energetic emulsifying means, such as
ultrasound, colloid mill or high-pressure homogenizer,
and

20 b) the polymerization of the said mixture at
a temperature ranging from 20 to 100°C using radical
initiators,

the level of organic cosolvent being less
than 0.2% by weight of the total weight of the
25 emulsion.

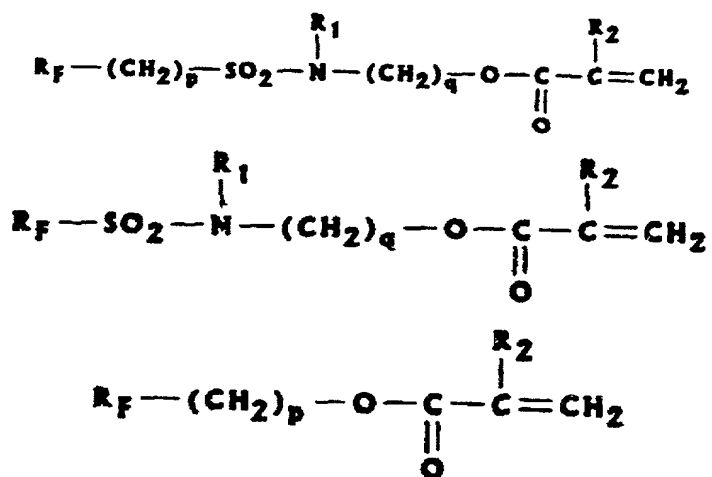
2. Process according to Claim 1,
characterized in that the mixture of monomers is

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stabilized by at least one surfactant chosen from the group comprising nonionic, anionic or cationic surfactants, such as polyethoxylated sulphosuccinate derivatives or quaternary ammonium derivatives.

- 5 3. Process according to Claim 1 or 2, characterized in that the fluorinated monomer A is chosen from the group comprising the monomers corresponding to the following formulae:

10



in which R_F represents a perfluorinated radical with a linear or branched chain comprising 2 to 20 carbon atoms, p and q , which are identical or different, each represent an integer ranging from 1 to 20 and preferably from 1 to 4, R_1 represents a linear or branched alkyl radical comprising from 1 to 4 carbon atoms and R_2 represents a hydrogen atom or a methyl radical.

4. Process according to one of the preceding claims, characterized in that the monomer B is chosen from the group comprising:

- C₁-C₂₂ alkyl (meth)acrylates
- 5 - (meth)acrylates, the radical of which carries an oxyethylenated linkage
- vinyl monomers, such as vinyl chloride or vinyl acetate
- acrylic and methacrylic acids.

10 5. Process according to one of the preceding claims, characterized in that the initiator is chosen from the group comprising:

- peroxides
- persalts, such as persulphates
- 15 - azo compounds, such as 4,4'-azobis (4-cyanopentanoic acid).

6. Aqueous dispersion of fluorinated polymers as may be obtained according to the process of any one of the preceding claims, the content of organic
20 cosolvent of which is less than 0.2% by weight of the total weight of the emulsion and the level of coagulum being less than 1% by weight of the total weight of monomers.

7. Application of the aqueous dispersion of
25 Claim 6 in the hydrophobic and oleophobic treatment of various substrates, such as leather, textiles, fitted carpets, paper and construction materials.

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JC08 Rec'd PCT/PTO 11 MAY 2007

ABSTRACT

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FLUORINATED POLYMERS BY MINIEMULSION POLYMERIZATION

◆◆◆◆◆

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Inventors: Mr Denis TEMBOU NZUDIE
Mr Didier JUHUE
Mr Jean-Marc CORPART

◆◆◆◆◆

The invention discloses a process for the preparation of fluorinated polymers by miniemulsion polymerization of a mixture of fluorinated and nonfluorinated monomers in the absence of organic solvent.

This polymerization process makes it possible to obtain an aqueous emulsion of fluorinated polymers devoid of coagulum.

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FOI-180-5257860

Declaration and Power of Attorney United States Patent Application

UNITED STATES
Patents and Design Patents
Sole & Joint Inventors
Convention & Non-convention
PCT & Non-PCT
This form cannot be amended, altered
or changed after it is signed.
(For use only for inventors who
understand the English language.)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **POLYMERS FLUORINATED BY POLYMERISATION IN MINI-**

EMULSION

(check one) ☒ is attached hereto.

☐ was filed as U.S. Application No. _____ on _____ and (if applicable) was amended on _____.

☐ was filed as PCT International Application No. _____ on _____ and (if applicable) was amended under PCT Article 34 on _____.

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or §365(b) of any foreign and PCT application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America listed in this Declaration. I have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application(s) on which priority is claimed:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)
98/14272	France	11/13/98	YES

I hereby claim the benefit under Title 35, United States Code, §120 or §365(c) of any United States application and PCT international application designating the United States of America listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

The duty is acknowledged for the Preliminary Amendment, which is hereby incorporated by reference as part of the original disclosure.

I hereby claim priority benefits under Title 35 United States Code §119(e) of any U.S. provisional application(s) listed below:

U.S. Provisional Application No.	Filing Date

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Robert G. Weilacher (20,531), Herbert M. Hanegan (25,682), Dale Lischer (28,438), Frederick F. Calvetti (28,557), J. Rodgers Lunsford, III (29,405), Michael A. Makuch (32,263), Dennis C. Rodgers (32,936), William F. Rauchholz (34,701), Michael K. Carrier (42,391), Eric J. Hanson (44,738), Patrick R. Delaney (45,338), and Brandon S. Boss (46,567).

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Additional inventors and/or prior applications are listed in attached Supplemental Sheet(s).

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21/06/2001

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